1. Title of the thesis:

Studies on Some Multiatomic Metal Oxy Ions Utilizing a Micro-Extraction and Subsequent Fourier Transform Infrared Spectroscopic Analysis

2. Introduction:

Infrared (IR) spectroscopy is a simplest and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long term unattended measurements. A common laboratory instrument that uses this technique is a Fourier Transform infrared (FTIR) spectrometer (Berthomeieu and Hienerwadel 2009). Further, the advent of hyphenating Fourier Transform technique with IR has improved its utility for the simple reason of practically instant analysis and possibilities of manipulating spectral scans. Mainly, FTIR has been used for the qualitative functional group identification of the organic compounds and structural elucidation. Incredibly, recent studies revealed important application of FTIR in the determination of inorganic chemical species such as etc. NH_4^+, SO_4^{2-}, NO_3^- in airborne solids (Kouyomdjian and Saliba 2005).

There are many types of metal oxy ions that remain in the form of their salts or in more complex form, in the environment. These particles in environment, having various types of direct and indirect effects on human and plants need be quantified. The determination of very low concentrations of inorganic and metal oxy ions in "unexposed" biological material (animal and human tissues, blood, urine, food) and environmental samples (air, water, soil and sediment) is extremely difficult and such problems still need to be solved. An accurate assessment of human exposure and nutritional requirements depends on reliable analytical results. Some metal oxy-anions such as $Cr_2O_7^{2-}$, $Cr_2O_4^{2-}$, CrO_4^{2-}, MoO_7^{2-}, AsO_4^{3-}, VO_4^{3-}, SeO_3^{2-} etc have unique property of changing dipole moment direction as a result of molecular vibration (Verma and Deb 2009; Verma *et al.* 2009) an indispensable property that may enable these species to be identified qualitatively as well as be determined quantitatively on interaction with electromagnetic radiation in infrared spectroscopic region. All multiatomic ions are infrared active and show vibrational bands in specific region. This unique characteristic behavior of these ions will be explored during proposed investigation, or their qualitative and quantitative analysis, by the diffuse reflectance(DRS)-Fourier transform infrared(FTIR) technique. Thus, the need for new procedures on determination of metal oxy ions with low detection

limit, high sample throughput, applicability to low sample size etc., in biological samples as well as in other environmental samples wherein sample size is a real challenge to the chemist, is a perpetual demand for the purpose of clinical diagnosis. Since earlier techniques reported for determinations of these species have drawbacks like use of large volumes of toxic solvents, poor detection limits and sample throughput values and need of large sample size, the proposed technique, i.e., DRS-FTIR with (for metal oxy anions) or without (for oxy-anions and cations) the combination of SDME will be tested for the first time ever to overcome most of the above shortcomings.

Even though excellent developments in the modern analytical instrument, which allocate enormous enrichment in aspects of analysis, in many cases the existing analytical instrumentation does not have as much as necessary sensitivity for the analysis of natural samples and or sometimes matrix interface causes difficulties in quantitative analysis of real samples.

In the present work, some of the multiatomic metal oxy ions, non metal oxy anions and gaseous non metal oxides will be tested for the qualitative identification and quantitative determination employing newly developed Single Drop Micro Extraction–Diffuse Fourier Transform Infrared Spectroscopy (SDME-DRS-FTIR) Technique. The method will also employ in the some real sample such as biological materials (animal and human tissues, blood, urine, food) and environmental samples (aerosols). We would also apply this method for study of the application of some metal nanoparticals.

3. A brief review of the work already done in the field:

Recent investigation shows that FTIR has been shown to be useful tool for qualitative and quasi-qualitative determination of inorganic species such as NH_4^+, SO_4^{2-}, NO_3^-, etc. (Kouyomdjian and Saliba 2005). Application of FTIR spectroscopy in environmental studies supported by tow dimensional correlation analysis has done by Mecozzi *et al.* 2009. FTIR spectroscopy allows the analysis of a relevant amount of compositional and structural information concerning environmental samples and joint use with 2DCORR has improved the performance of this technique in the studies of complex environmental systems (Noda and Ozaki 2005). FTIR spectroscopy is recently used in different analytical methods such as study of petroleum Heat-exchanger deposit (Tay and Kazarian 2009), investigation of coal component of Late Permian coals from Southern China (Wang *et al.* 2011). Fatty acid compositions were quantitatively determined in micro-encapsulated fish-oil supplements using FTIR (Vongsvivut *et al.* 2012). FTIR spectroscopy is also used for the comparative analysis of

smokeless gunpowdwers (Lopez-Lopez *et al.* 2012). Chou *et al.* 2005, have shown the application of FTIR for size-segregated characterization of atmospheric aerosol. The quantitative analysis of vergin coconut oil in cream cosmetics preparation was done using FTIR (Rohman *et al.* 2009). FTIR were used for the analysis of pork adulteration in beef meatball (Rohman *et al.* 2011). Tasi and kuo have developed the diffuse reflectance infrared Fourier transform spectroscopic method for rapid characterization of aeroslos (Tasi and Kuo 2006). The Rapid discrimination of pork in Halal and non-Halal Chinese ham sausages by Fourier transform infrared (FTIR) spectroscopy and chemometrics (Xu *et al.* 2012). The FTIR spectroscopic imaging and multivariate regression for prediction of proteoglycan content of articular cartilage is reported earlier (Rieppo *et al.* 2012). Recently, the Passive detection of biological aerosols in the atmosphere with a Fourier Transform Instrument (FTIR)-the results of the measurements in the laboratory and in the field was studied (Blecka *et al.* 2012).

Modern analytical chemistry is dominated by instrumental analysis. Many analytical chemists focus on a single type of instrument. Academics tend to either focus on new applications and discoveries or on new methods of analysis. The discovery of a chemical present in blood that increases the risk of cancer would be a discovery that an analytical chemist might be involved in. Many methods, once developed, are kept purposely static so that data can be compared over long periods of time. This is particularly true in industrial quality assurance (QA), forensic and environmental applications.

As it has been already reported that metals in environmental sample is generally determined by spectrophotometric methods which employ a color reaction of metal with organic and inorganic reagent but the concentration of reagent and pH affect the color development (Thakur and Deb 1999). There are many other methods such as fluorimetry (Jie *et al.* 1998), thin layer chromatography (Mohammad *et al.* 2000), capillary electrophoresis (O'Reilly *et al.* 2001) and induced flow injection analysis (Simkin *et al.* 2004). Instead of these, the flame atomic absorption spectroscopy (FAAS) (Melo *et al.* 2000), inductive coupled plasma atomic emission spectrometry (ICP-AES) (Boevski *et al.* 2000), and inductive coupled plasma mass spectrometry (ICP-MS) (Xia *et al.* 2005) are accessible for the determination of trace metal with enough sensitivity for most applications. These methods are only suitable for relatively large sample volumes.

In many common analytical methods, the volume of the sample is very small. In GC, HPLC and graphite furnace atomic adsorption spectrometry (GF - AAS), this volume is usually around 5-20 µL, while in diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR) it is found to be around 3-10 µL. The chromatographic techniques often suffer from disadvantages such as incomplete derivatization, being time-consuming and entailing complicated operating procedures. The determination of inorganic and metal oxy-anions using GF-AAS have also some limitations in terms of high cost of instruments used in routine analysis, matrix effects, effect of temperature, reagent ratios, cooling time and required special type furnace tube. Several procedures have been developed for the separation and pre-concentration of contaminants from environmental matrices, such as: liquid-liquid extraction (LLE) (Anthemidis *et al.* 2003), co-precipitation (Gueguen *et al.* 2001). However, disadvantages such as significant chemical additives, solvent losses, large secondary wastes, unsatisfactory enrichment factors and high time consumption, limit the application of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and pre-concentration without complex processes. The solvent micro-extraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and pre-concentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrices. Solvent micro-extraction like technique, viz., single drop micro-extraction (SDME) is a form of solvent extraction with phase ratio values higher than 100. A review on recent advances in various applications of SDME technique is reported (Jain and Verma 2011). Compared with the conventional solvent extraction, micro-extraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances and thus the detection limit may go down further. In addition, the amount of the used organic solvent is highly reduced and only one step of manipulation is necessary, therefore, problems of contamination and loss of analytes vanishes.

4. Objectives:

The specific objectives of the proposed work may be summarized as follows:

- Detection of important IR active chemical species in environmental view point at very low level by proper selection of qualitative analytical peaks in infrared region and preparing a library finger print sniffing database.

- Determination of the metal contents in the multiatomic oxy-anionic and cationic chemical species (e.g. $Cr_2O_7^{2-}$, $Cr_2O_4^{2-}$, CrO_4^{2-}, MoO_7^{2-}, MnO_4^{-}, AsO_4^{2-}, AsO_4^{3-}, OsO_5^{2-}, VO_4^{3-}, SeO_3^{2-}) at trace level employing micro or single drop micro extraction (SDME) and DRS-FTIR technique on KBr or zinc selenide substrates.
- Test of analytical quality assurance (AQA) and statistical and varimax principal component analysis (PCA) for simultaneous analysis in real samples.
- Application of the newly developed method to some real samples where available sample size is extremely low e.g. biological material (animal and human blood and fluids) and environmental samples (aerosols).

5. Noteworthy contribution in the field of proposed work:

Keeping in mind the fact that FTIR could provide as an effective and powerful tool for quantitative analysis as well, Verma and Deb have recently employed diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR) for sensitive determination of inorganic species like nitrate (NO_3^-) and sulphate (SO_4^{2-}) functional groups in the environmental samples (Deb and Verma 2010; Verma and Deb 2007a, b). These methods are extremely rapid, highly sensitive, reproducible and more interestingly non-destructive. Vanadium(V) and chromium(VI) (Figure 1) have been successfully determined employing new combined single-drop micro-extraction and diffuse reflectance FTIR technique (Verma and Deb 2009; Verma *et al.* 2009). Vrema and Deb also determine nitrogen dioxide (Figure 2) in the ambient air by diffuse reflectance FTIR technique (Verma *et al.* 2008). The exclusion of nitrogen from sample matrix by zirovalent iron nanoparticles and determination of ammonium has been effectively done by FTIR (Deb and Verma 2009).

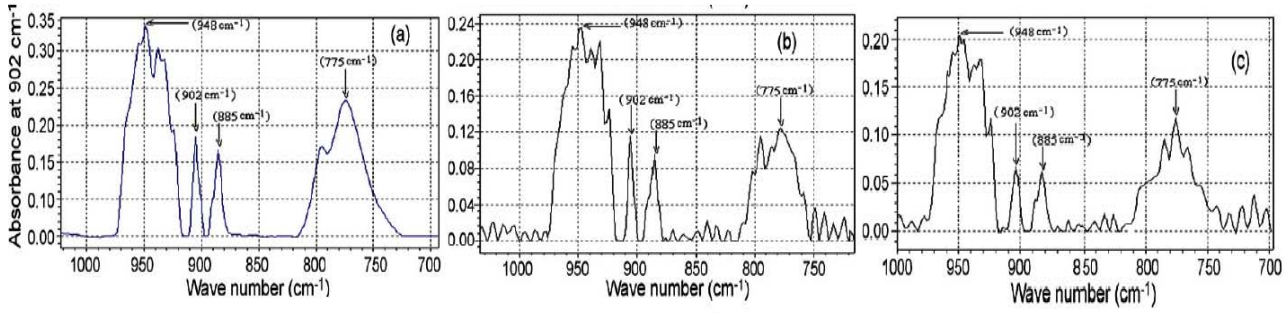


Figure 1: DRS-FTIR spectra of dichromate; before (a) and after extraction with HOA (b),i.e., $Cr_2O_7^{2-}$ in its purest form and in complexed form, and $Cr_2O_7^{2-}$–HOA complex extracted by SDME process from a real human blood serum sample (c). (Verma *et al.* 2009)

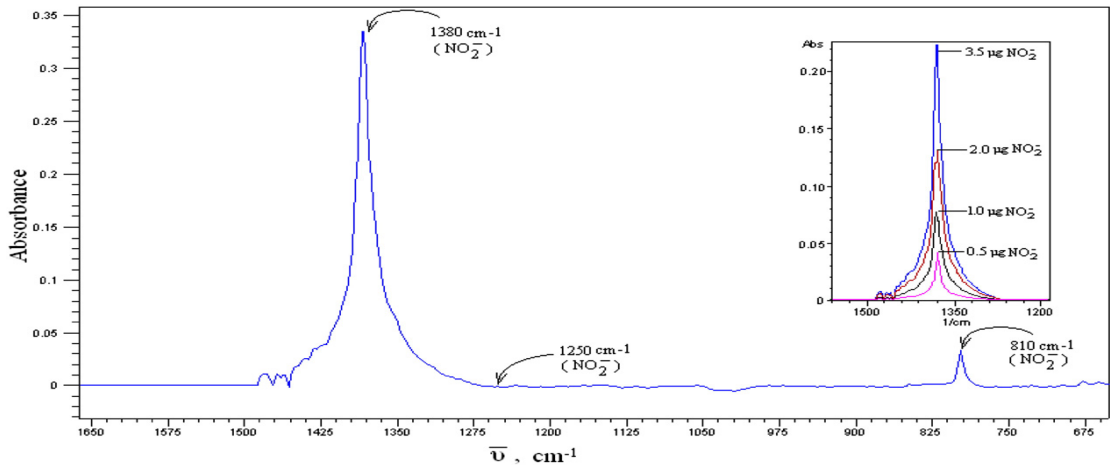


Figure 2: Quantitative IR reflectance spectra converted into Kubelka Munk spectrum for smoothing of the baseline (Verma *et al.* 2008).

Amidines (Deb *et al.* 1990) and hydroxyamidines (Chakravarty *et al.* 1993; Thakur and Deb 1999) have been used for macro amount solvent extraction and spectrophotometric determination of metals like Cr, Cu, Mo, V, As etc. in the form of binary or ternary complexes in the past in our laboratory. Utilizing this basic chemistry, as a preliminary investigation, it has been observed that the DRS-FTIR spectral scans of the pure dichromate ($Cr_2O_7^{2-}$) in KBr substrate has almost no difference in spectral positions with its hydroxyamidine (HOA) complex extracted in single drop in dichloromethane and spiked on KBr substrate. This indicates that such metallic-ionic species does not lose their identity even after complexation with organic ligand. This has opened an innovative avenue for us to develop single drop micro-extraction procedure for metallic species with different organic ligands and subsequent FTIR/ DRS-FTIR quantification of such chemical species.

6. Proposed methodology:

(A) *Micro-Extraction (ME)*

Micro-extraction techniques such as single drop micro-extraction (SDME) with subsequent DRS-FTIR technique shall be applied for trace detection and determination of metal pollutants like $Cr_2O_7^{2-}$, MoO_7^{2-}, MnO_4^- etc. SDME is relatively a better technique than the traditional solvent-extraction chemistry in many ways such as the least requirement of chemicals, avoiding handling of large volume of toxic solvents (particularly for trace detection and determination), high sensitivity of the method etc.

With the help of micro-syringe tips extraction of some of the multiatomic metallic ionic species like $Cr_2O_7^{2-}$, MoO_4^{2-} will be done. Organic ligands e.g. amidine, hydroxyamidine or other ligands prepared in polar or non-polar organic solvents shall be delivered through the micro-syringe tips into the extraction vessel containing standard solutions of the metal ions. The micro drop either just at the micro syringe tip or at the bottom of the vessel shall be allowed to remain for ampoule amount of time so that extraction of metal ion into the micro drop is complete upon sufficient stirring. The micro-drop-complex shall be withdrawn back through the syringe carefully and shall be retained for further analytical work. The SDME processes will be done either for the already established systems or for some new systems. Figure 3 shows the schematic diagram of SDME process. Table (1) shows some of the characteristic features of the traditional solvent extraction of some selected metal ions reported earlier (Chakravarty *et al.* 1993; Thakur and Deb 1999).

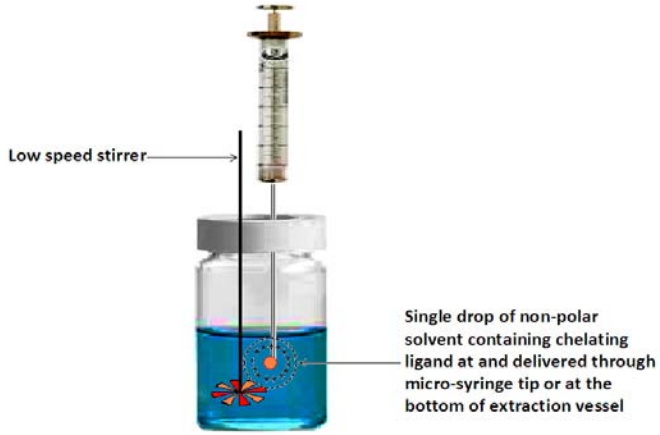

Low speed stirrer
Single drop of non-polar solvent containing chelating ligand at and delivered through micro-syringe tip or at the bottom of extraction vessel

Figure 3: Formation of electrical double-layer between charged metallic species (e.g. $Cr_2O_7^{2-}$) in aqueous medium and extracting ligand (e.g. HOA) in non-polar solvent just before occurrence of single drop micro-extraction.

Table 1: Chemistry of LLE of some of the metal oxy anions reported earlier in our laboratory.

Metaloxy anions	Extracting reagents	Stoichiometry	Extracting solvents
Arsenic(AsO^{2-})	*N, N'*-Diphenylbenzamidine (DPBA)	1:4:2 (As(III) : I^- : DPBA)	1-Pentanol, ethyl acetate, isomethyl butyl ketone
Osmium(OsO_5^{2-})	*N*-Hydroxy-*N, N'* - Diphenylbenzamidine (HOA)	1:2:2 (Os : $Ar(OH)_2$: HOA)	1-Pentanol, ethyl acetate,o-dichlorobenzene
Vanadium(VO_4^{3-})	*N*-Hydroxy-*N, N'* – Diphenylbenzamidine (HOA)	1:2:1 (V:HOA:NO_2PhOH)	1-Pentanol, ethyl acetate, isomethyl butyl ketone, carbon tetra-chloride, cyclohexane
Chromium($Cr_2O_7^{2-}$)	*N*-Hydroxy-*N, N'* – Diphenylbenzamidine (HOA)	1:2 (Cr:HOA)	Ethyl acetate, carbon tetrachloride

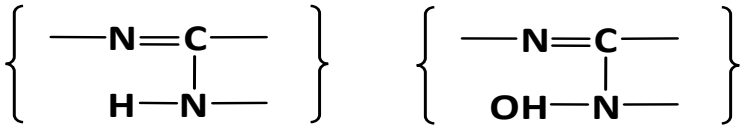
- ***pH and acidity for extraction***

The pH and acidity is a very important parameter for the extraction process. A suitable pH or acidity is required for the different metallic extraction process. Different buffer solutions or mineral acids like HCl, H_2SO_4, HNO_3 etc. will be used for such purpose.

- ***Extracting agent and reagent range***

The reagent concentration range for complete formation and extraction into suitable solvents of the complexes will be studied for optimization of analytical condition. Hydroxyamidines(HOA), and amidines(HA) in the concentration range 0.10-0.15 % have been reported as versatile reagents for gravimetric as well as colorimetric estimation of various metals e.g. iron, vanadium, bismuth, chromium, antimony, arsenic, tungsten, rhenium, gold etc.

Amidines (Deb *et al.* 1990) and hydroxyamidines (Chakravarty *et al.* 1993; Thakur and Deb 1999) contain groups as shown below. These reagents form binary and ternary complexes with metals, extractable into various organic solvents. Effective extraction of metals with enhanced selectivity and sensitivity are the special features of these reagents. It is also proved in some cases that they prevent metals from hydrolysis. Amidines and hydroxyamidines are very stable towards light and heat, and their solution in various organic solvents can be stored for a long period without any deterioration.



- ***Stoichiometry of the complex***

The stoichiometry of the metal complexes will be studied spectrophotometrically by the standard methods *viz.* Job's method of continuous variation, mole ratio method, etc.

(B) ***DRS-FTIR Determination of Multiatomic Metal oxy ionic Species***

The spectral studies of SDME extracted multiatomic metal oxy-anionic species (e.g. $Cr_2O_7^{2-}$, MoO_7^{2-}, MnO_4^- etc.) into suitable solvent with chelating agent will be done using DRS-FTIR on KBr matrix or in a zinc selenide substrate. The DRS will be employed separately to check the differences in sensitivity of the methods.

- ***Subsequent micro-extraction analysis in KBr / Zinc selenide substrate***

In our preliminary investigation, we used infrared spectrometric grade KBr as a matrix for the analysis, wherein all standards were poured into the finely ground and pre-weighed KBr for the matrix formation. This matrix was applied to the DRS directly for the spectral scanning. It was observed, interestingly, that there were no changes in the spectral position of the respective vibrational mode of chemical species when used as standard solution directly or after extraction with hydroxyamidine like complexing or chelating agents. This has shown the retention of the structural identity of such species even after complexation. The above scheme will be used also in the current research work for different chemical species. Comparative studies with different substrates like KBr and zinc selenide will be done to check sensitivity differences.

- ***Baseline correction for qualitative and quantitative analytical peaks***

On eyeballing to the spectral peaks to be obtained, qualitative as well as quantitative analytical peaks will be selected on the basis of simple reasons of sharp and intense spectral peaks in the observed regions of the IR scan. Further, for qualitative or quantitative analysis a two-point or multiple-point baseline corrections will be done in the selected region of IR scan. Table 2 shows infrared absorption bands and different modes of vibration for some of the multi atomic species.

- **Data acquisition and statistical analysis**

1. For collection of spectral data for the species under investigation the following manipulating tools will be applied such as: Data set, purity, deconvolution, FFT, Kubelka Munk, ATR correction, Kramers Kronig (to separate the reflectance spectrum into an absorption spectrum and a refractive index spectrum in order to facilitate spectral analysis), peak split, atmosphere correction, arithmetic, normalized, baseline (zero, three, multiple point), smoothing, derivative.
2. To analyze method multipoint, PLS based on principal component analysis (PCA), advantageous in that the problem of colinearity is overcome, would be employed.
3. Evaluation method for calibration: Internal validation method employing a standard sample to evaluate the calibration.
4. Determination of LOD, LOQ, LDR, test of Analytical Quality Assurance (AQA) employing significance parameters such as F- and T-tests.

Table 2: Infrared absorption bands and different modes of vibrations for some of the multiatomic metal oxy-anions

Ionic Species	Vibrational modes	Absorption peak range Reported (cm^{-1})
Dichromate ($Cr_2O_7^{2-}$)	Asymmetric stretching (υ_3)	880- 990 (Strong)
	Symmetric stretching (υ_1)	720-840 (Strong)
	Bending vibrations (υ_4)	340-380 (Weak)
	Bending vibrations (υ_2)	
Chromite ($Cr_2O_4^{2-}$)	-	620-720 (Strong)
		515-550 (M Strong)
Chromate (CrO_4^{2-})	Symmetric stretching (υ_1)	850-930 (Strong)
	Asymmetric stretching (υ_3)	
Molybdate (MoO_4^{2-})	Symmetric stretching (υ_1)	750-970 (Strong)
	Asymmetric stretching (υ_3)	(940, 895)
	Bending vibrations (υ_4)	308-350 (Weak)
	Bending vibrations (υ_2)	(365, 220)
Selenite (SeO_3^{2-})	Asymmetric stretching (υ_3)	770-700 (Strong)
	Bending vibrations (υ_2)	540-430 (Strong)
	Bending vibrations (υ_4)	420- 380
Selenate (SeO_4^{2-})	Symmetric stretching (υ_1)	910-840 (Strong)
	Asymmetric stretching (υ_3)	(833, 875)
	Bending vibrations (υ_2)	450-330 (Weak)
	Bending vibrations (υ_4)	(335, 432)
Orthoarsenate (AsO_4^{3-})	Symmetric stretching (υ_1)	850-770 (Strong)
	Asymmetric stretching (υ_3)	(813)
	Bending vibrations (υ_2)	550-400 (Medium)
	Bending vibrations (υ_4)	(402, 342)
Vanadate (VO_4^{2-})	Asymmetric stretching (υ_3)	900-700 (Strong)
	Symmetric stretching (υ_1)	(870, 825)
	Bending vibrations (υ_2)	490-300 (medium)
	Bending vibrations (υ_4)	(345, 480)

7. Expected outcome of the proposed work:

1. The proposed work will be done in micro level so the requirements of the chemicals and reagents will be very less. Thus this technique will be highly economic and cost-effective. In addition, the proposed work will also meet to the present-day-challenge of 'green-chemistry' which demands for creation of no or little pollution.
2. In some cases the analysis may be even non-destructive. This may be helpful for analysis of those samples whose physical forms need to be retained for advanced or other kind of analysis.

3. The magnificence of the present work will remain with the need of very low volume and size of samples i.e. ~ 3-10 µg or 3-10 µl will be required for the analysis. The sample throughput of the technique will be of high magnitude due to almost instantaneous recording of data.
4. Single drop micro extraction (SDME) will enhance the selectivity of the method and also it will allow very low amounts of reagents.
5. Importantly, this work will open an avenue for the use of FTIR as an effective and simple analytical tool in the fields of micro determination chemistry.

8. References:

Anthemidis AN, Zachariadis GA, Stratis JA; *J. Anal. At. Spectrom.* **18** (2003) 1400.

Berthomieu C, Hienerwadel R; *Photosynth Res.* **101** (2009) 157.

Błęcka MI, Rataj M, Szymański G; *Orig Life Evol Biosph* **42** (2012) 101.

Boevski I, Daskalova N, Havezov FI, *Spectrochim. Acta Part B,* **55** (2000) 1643.

Chakravarty S, Deb MK, Mishra MK; *J. Assoc. Offic. Anal. Chem*. **76** (1993) 604.

Chou CCK, Huang SH, Chen TK, Lin CY, Wang LC; *Atmos. Res.*, **75** (2005) 89.

Deb MK, Agarwal C, Patel KS, Mishra RK; *Intern. J. Environ. Anal. Chem.* **39** (1990) 417.

Deb MK, Verma D; *Microchim. Acta* **169** (2010) 23.

Gueguen C, Dominik J, Perret D; *Fresen. J. Anal. Chem.* **370** (2001) 909.

Jain A, Verma KK; *Anal. Chim. Acta* **706** (2011) 37.

Jie N, Yang D, Zhang Q, Yang J, Song Z; *Anal. Chim. Acta,* **359 (**1998) 87.

Kouyomdjian H, Saliba NA; *Atmos. Chem. Phy. Discuss.* **5** (2005) 13053.

López-Lópeza M, Ferrandoa JL, García-Ruiz C; *Analytica Chimica Acta.* **717** (2012) 92.

Mecozzi M, Moscato F, Pietroletti M, Quarto F, Oteri F, Cicero AM; *Global Nest Journal* **11** (2009) 593.

Melo MHA. Ferreira SLC, Santelli RE; *Microchem. J.* **65** (2000) 59.

Mohammad A, Chahar JPS, Iraqi E, Agrawal V; *J. Plan. Chromatogr. Mod. TLC* **13** (2000) 12.

Nada I, Ozaki I; John Wiley & Sons, UK (2005).

O'Reilly JW, Dicinoski GW, Shaw MJ, Haddad PR; *Anal. Chim. Acta* **432** (2001) 165.

Rieppo L, Rieppo J, Jurvelin JS, Saarakkala S; *PLoS One* **7** (2012) 32344.

Rohman A, Man YC, Sismindari; *Pak J Pharm Sci*. **22** (2009) 415.

Rohman A, Sismindari, Erwanto Y, Che Man YB; *Meat Sci*. **88** (2011) 91.

Simkin SM, Lewis DN, Weathers KC, Lovett GM, Schwarz K; *Water Air and Soil Polltn.* **153** (2004) 343.

Tay FH, Kazarian SG; *Energy & Fuels* **23** (2009) 4059.

Thakur M, Deb MK; *Talanta* **49** (1999) 561.

Thakur M, Deb MK; *The Analyst* **124** (1999a) 1331.

Tsai YI, Kuo SC ; *Atmos. Environ.,* **40 (**2006) 1781.

Verma D, Deb MK; *J. Environ. Anal. Chem.* (2009)

Verma SK, Deb MK, Verma D; *Atmospheric Research* **90** (2008) 33.

Verma SK, Deb MK; *Anal. Chim. Acta* **582** (2007b) 382.

Verma SK, Deb MK; *Talanta* **71** (2007a) 1546.

Verma SK, Deb MK; *Talanta* **78** (2009) 70.

Vongsvivut J, Heraud P, Zhang W, Kralovec JA, McNaughton D, Barrow CJ; *Food Chem* **135** (2012) 603.

Wang S, Tang Y, Schobert HH, Guo Y, Su Y; *Energy Fuels* **25** (2011) 5672.

Xia L, Hu B, Jiang Z, Wu Y, Li L, Chen R, *J. Anal. At. Spectrom*. **20** (2005) 441.

Xu L, Cai CB, Cui HF, Ye ZH, Yu XP; *Meat Sci*. **92** (2012) 506.

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